OPTIMIZATION OF SOLUTION POLYMERIZATION OF METHYL METHACRYLATE

LAW WOON PHUI

UNIVERSITI MALAYSIA PAHANG

OPTIMIZATION OF SOLUTION POLYMERIZATION OF METHYL METHACRYLATE

LAW WOON PHUI

Thesis submitted in partial fulfillment of the requirements

for the award of the degree of Bachelor of Chemical Engineering

Faculty of Chemical and Natural Resources Engineering

UNIVERSITI MALAYSIA PAHANG

FEBRUARY 2013

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

NOMENCLATURE

A	Reactor-jacket heat transfer area, m^2
$A(T)$	Temperature dependent constant in gel effect model
B	Constant in gel effect model
C	Heat capacity of reactant mixture, kJ kg^{-1} K^{-1}
C_i	Concentration of initiator, kgmole m^{-3}
$C_i^*(0)$	Optimal initial concentration of initiator, kgmole m^{-3}
C_m	Concentration of monomer, kgmole m^{-3}
$C_m^*(0)$	Optimal initial concentration of monomer, kgmole m^{-3}
C_s	Concentration of solvent, kgmole m^{-3}
C_w	Heat capacity of water, kJ kg^{-1} K^{-1}
D_n	Dead polymer chain with n unit of monomers
E_i, E_p	Activation energy for initiation and propagation reactions, kJ $kgmole^{-1}$
E_{fm}, E_{fs}	Activation energy for chain transfer to monomer and solvent reactions, kJ $kgmole^{-1}$
E_{po}, E_{to}	Activation energy for the k_{po} and k_{to} respectively, kJ $kgmole^{-1}$
$E_{\Theta t}$, $E_{\Theta p}$	Activation energy for the $k_{\Theta t}$ and $k_{\Theta p}$ respectively, kJ $kgmole^{-1}$
f	Efficiency of initiator
F_{cw}	Inlet flow rate of cooling water, m^3 s^{-1}
F_{cwmax}	Maximum inlet flow rate of cooling water, m^3 s^{-1}
I	Initiator
k_{fm}, k_p	Rate constants for chain transfer to monomer and propagation reactions, m^3 $kgmole^{-1}$ s^{-1}
k_{tc}, k_{td}	Rate constants for termination by combination and disproportionation reactions, m^3 $kgmole^{-1}$ s^{-1}
k_{po}, k_{to}	Overall propagation and termination rate constants at zero monomer conversion, m^3 $kgmole^{-1}$ s^{-1}
k_i	Rate constant for initiation reaction, s^{-1}
$k_{\Theta p}$	Temperature dependent constant in gel effect model

$k_{\Theta t}$	Temperature and initiator loading concentration dependent parameter in gel effect model
m	Weight of reactant mixture, kg
M	Monomer
M_i	Molecular weight of initiator, kg kgmole^{-1}
M_m	Molecular weight of monomer, kg kgmole^{-1}
M_n	Number-average molecular weight of dead polymer, kg kgmole^{-1}
M_s	Molecular weight of solvent, kg kgmole^{-1}
M_w	Weight-average molecular weight of dead polymer, kg kgmole^{-1}
P	Input power to heater, kJ s^{-1}
P_{max}	Maximum power of heater, kJ s^{-1}
P_n	Live polymer chain consisting of n monomer units
R	Universal gas constant, kJ kgmole^{-1} K^{-1}
R_m, R_i	Rate of production of M and I, kgmole m^{-3} s^{-1}
S	Solvent
t	Time, s
t_f	Terminal time, s
$T(t)$	Reactor temperature profile, K
T_o	Initial reactor temperature, K
$T^*(t)$	Optimal reactor temperature profile, K
T_{cw}	Temperature of cooling water, K
T_∞	Room temperature, K
T_{gp}	Glass transition temperature of PMMA, K
T_j	Jacket temperature, K
T_{jo}	Initial jacket temperature, K
$\hat{U}$	Single manipulated input obtained by coordinating the two actual manipulated inputs (P and F_{cw})
V	Volume of reactant mixture, m^3
V_o	Initial volume of the reactant mixture, m^3
X_m	Monomer conversion
Z_i	Frequency factor for initiation reaction, s^{-1}
Z_{fm}, Z_{fs}	Frequency factors for chain transfer to monomer and solvent reactions, m^3 kgmole^{-1} s^{-1}
Z_{po}, Z_{to}	Frequency factors for k_{po} and k_{to}, m^3 kgmole^{-1} s^{-1}

$Z_{\Theta t}$, $Z_{\Theta p}$	Frequency factors for parameters $k_{\Theta t}$ and $k_{\Theta p}$, m^3 $kgmole^{-1}$ s^{-1}
$-\Delta H_p$	Heat of propagation reactions, kJ $kgmole^{-1}$
ε	Volume expansion factor
α	Process parameter
Φ_{mo}	Initial volume fraction of monomer
μ_1	Mass concentration of dead polymer chains, kg m^{-3}
ρ	Overall density of reactant mixture, kg m^{-3}
ρ_i	Density of initiator, kg m^{-3}
ρ_s	Density of solvent, kg m^{-3}
ρ_m	Density of monomer, kg m^{-3}
ρ_w	Density of water, kg m^{-3}

PENGOPTIMUMAN BAGI METHYL METHACRYLATE LARUTAN POLIMERISASI

ABSTRAK

Dalam kajian ini, pengoptimuman untuk dinamik reaktor dan jaket telah dijalankan bagi MMA larutan polimerisasi dengan toluena di kelompok reaktor. Tujuan kajian ini dilaksanakan adalah untuk mengoptimumkan keadaan proses polimerisasi supaya mendapatkan pengubahan yang maksimum dalam masa yang singkat. Kesan gel, kesan kaca, kinetik bukan linear dan tindakbalas yang eksoterma dipertimbangkan dalam proses pengoptimuman. Kecekapan pemula dan pekali pemindaan haba keseluruhan diandaikan kekal malar. Pengoptimuman bagi MMA larutan polimerisasi berdasarkan model tiga peringkat polimerisasi dengan menggunakan perisian MATLAB. Penyelesai Ode23t digunakan dalam menyelesaikan masalah yang serdehana sengit. Keputusan menunjukkan bahawa pengubahan yang tinggi dapat diperolehi pada keadaan dimana kepekatan pemula (AIBN), suhu reaktor dan suhu jaket yang optima. Simulasi bagi MMA larutan polimerisasi dalam kajian ini menunjukkan bahawa MATLAB adalah alat penyelesai yang berkesan dan ekonomi dalam kerja-kerja kejuruteraan.

OPTIMIZATION OF SOLUTION POLYMERIZATION OF METHYL METHACRYLATE

ABSTRACT

In this study, optimization of reactor and jacket dynamics were carried out for the solution polymerization of MMA with toluene in batch reactor. The purpose of this study is to optimize the process condition in polymerization in order to obtain maximum conversion in minimum batch time. The gel effect, glass effect, non-linear kinetic and high exothermic reactions were considered. Initiator efficiency and overall heat transfer coefficient assumed remain constant. Optimization of MMA solution polymerization was based on three stage polymerization model (TSPM) by using MATLAB software. Ode23t solver was used in solving this moderate stiff problem. The results showed that high conversion was obtained at optimum concentration of initiator (AIBN), reactor temperature and jacket temperature. Simulation of the solution polymerization of MMA in this study showed that MATLAB was an effective and economical problem solving tools in engineering works.

CHAPTER 1

INTRODUCTION

1.1 Background of the Study

Polymer is a common materials widely used in household use, pipeline system, construction, transportation and medical technologies. A polymer is a macromolecule composed of repeating structural units. These sub-units were bonded by covalent force (Cowie and John, 1991). Polymer comprised of natural and synthetic polymers with a wide variety of properties. Natural polymers were such as natural rubber and cellulose which was the main constituent of wood and paper. Synthetic rubber, nylon, polyvinyl chloride (PVC), polystyrene, polymethyl methacrylate and silicone were the synthetic polymers (Lewis et al., 2004).

Methyl methacrylate (MMA) was an organic compound used as monomer to produce versatile polymethyl methacrylate (PMMA). MMA solution polymerization was a free radical chain reaction combine with hydrolysis process. Methanol, benzene, toluene and acetic acid were commonly used as solvent (Semsarzadeh et al., 1997). Polymerization included of three steps which were initiation, propagation and termination. Software was used in this study rather than laboratory testing due to its

low costs, no chemical waste, save time, high quality data available and no human error. Optimization of MMA polymerization depends on engineering variables such as temperature, molecular weight of polymer, monomer conversion, initiator concentration and batch time. Manipulated variables were temperature and initiator concentration. The controlled variables were the conversion of monomer.

1.2 Problem Statement

MMA had a big demand in the future and had a very steady growth. This was because PMMA had wide application in many fields such as construction materials, vehicles, signboard and high resistant plastic window such as windows of airplanes. Demand of product depended on quality of product itself. Condition in process can influenced the quality of product. Therefore, selection of best condition for different desired properties of product was the crucial part in optimization. Optimization of MMA solution polymerization was a complex process in chemical and biochemical industry due to its highly non-linear kinetic and exothermic reaction (Hyung-Jun et al., 1998) and (Baillagou and Soong, 1985). Since polymerization was a highly exothermic reaction, it induced a sudden increase in temperature and may cause the thermal runaway effect, low quality product, instabilities and even explosion. Therefore, it was important to control the temperature. Gel effect and glass effect acted as disturbances had been controlled to avoid undesired properties of final polymer product (Lepore et al., 2007). Monomer conversion and polymer molecular weight depended on initiator concentration and reaction temperature. Combination of right type of initiator with optimal composition and the temperature profile was

considered in kinetic control to avoid undesired residual and vaporization of monomer if temperature is too high (Gao et al., 2004).

1.3 Research Objectives

i. To develop solution polymerization optimization by using MATLAB.

ii. To optimize temperature and initiator concentration to obtain desired values of conversion in minimum batch time.

iii. Compare results with experimental work by Soroush and Kravaris (1992).

1.4 Scope of the Study

i. To optimize solution polymerization of methyl methacrylate with toluene in the presence of Azo Bis Isobutyronitrile (AIBN) as initiator by using batch reactor.

ii. MATLAB software based on three stage polymerization model (TSPM) was used to obtain optimal initiator concentration and reaction temperature.

iii. Compare with results from the journal by Soroush and Kravaris (1992).

1.5 Expected Outcome

i. Desired monomer conversion can be maximized.

ii. Initiator concentration and reaction temperature can be optimized.

iii. Final batch time for polymerization optimization can be minimized.

1.6 Significance of the Study

Optimization of MMA purposed to obtain the optimal values of condition parameters which can improved the properties of final polymer product. Also, the study was able to reduce the undesired waste generation which fulfill to manufacturer and customer's demand. Production expenditure was reduced due to the minimization on the batch time during the polymerization.

1.7 Conclusion

Polymer product was widely required especially in engineering field. In order to produce desired degree of polymer product, optimization of polymer properties was the crucial process. Efficient controlling of the optimal condition would give impacts on production time, quality, quantity and economic value to the industry.

CHAPTER 2

LITERATURE REVIEW

2.1 Methyl Methacrylate (MMA)

Methyl methacrylate (MMA), $C_5H_8O_2$ was a colourless, volatile organic compound with a characteristic odor that had been described as fragrant, fruity, acrid and pungent (National Industrial Chemicals Notification and Assessment Scheme, 2009). The purity of commercial MMA is typically 99.9%. It contained traces of acidity as the methacrylic acid and water (Dormer et al., 1998). Figure 2.1 shows the structural of MMA.

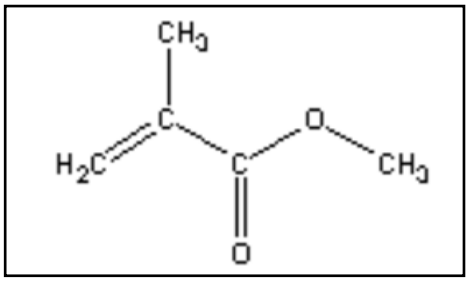

Figure 2.1 Structural of MMA

2.1.1 Chemical and Physical Properties of MMA

The physical and chemical properties of MMA were summarized in Table 2.1 (CHEMFATE, 1994; Ehrenstein, 2001; Evonik Industries AG, Keith and Walters, 1985; 2011; U.S. EPA, 1985; Verschueren, 1983).

Table 2.1 Chemical and Physical Properties of MMA

Properties	**Data**
Physical State	Liquid
Appearance	Colourless
Molecular Weight	100.12 g/gmol
Melting Point	- 48 ℃
Boiling Point	100-101 ℃
Critical Temperature	279 ^{o}C
Critical Pressure	37.5 bar
Critical Volume	0.32 m^3/mol
Water Solubility	15 g/L (25 ℃)
Density	0.939 g/cm ^{3}(20 ℃)
Vapor Density (air=1)	3.45 g/mL
Vapor Pressure	4 kPa (20 ℃)
Viscosity	0.6 cP (20 ℃)
Flash Point	10 ℃
Henry's Law Constant	$3.37x10^{-4}$ atm m^3/mol
Odor Threshold	0.2 mg/m^3
Flammability	Highly flammable

2.1.2 Synthesis of MMA

MMA was commercially manufactured by a number of routes. Figure 2.2 shows the routes to MMA. In acetone cyanohydrin (ACH) route, acetone and hydrogen cyanide were used as raw materials. MMA was produced from isobutylene (TBA) which was sequentially undergo two stage gas phase oxidation from TBA to

methacrylic acid, followed by esterification (Bauer, 2000). MMA could be prepared from methyl propionate and formaldehyde too (Nexant Chem System, 2006). For the new development, the Lucite-Alpha process relied on combined carbonylation and esterification of ethylene to methyl propionate. Methyl propionate reacted with formaldehyde under almost anhydrous conditions to form MMA (Nexant Chem System, 2006).

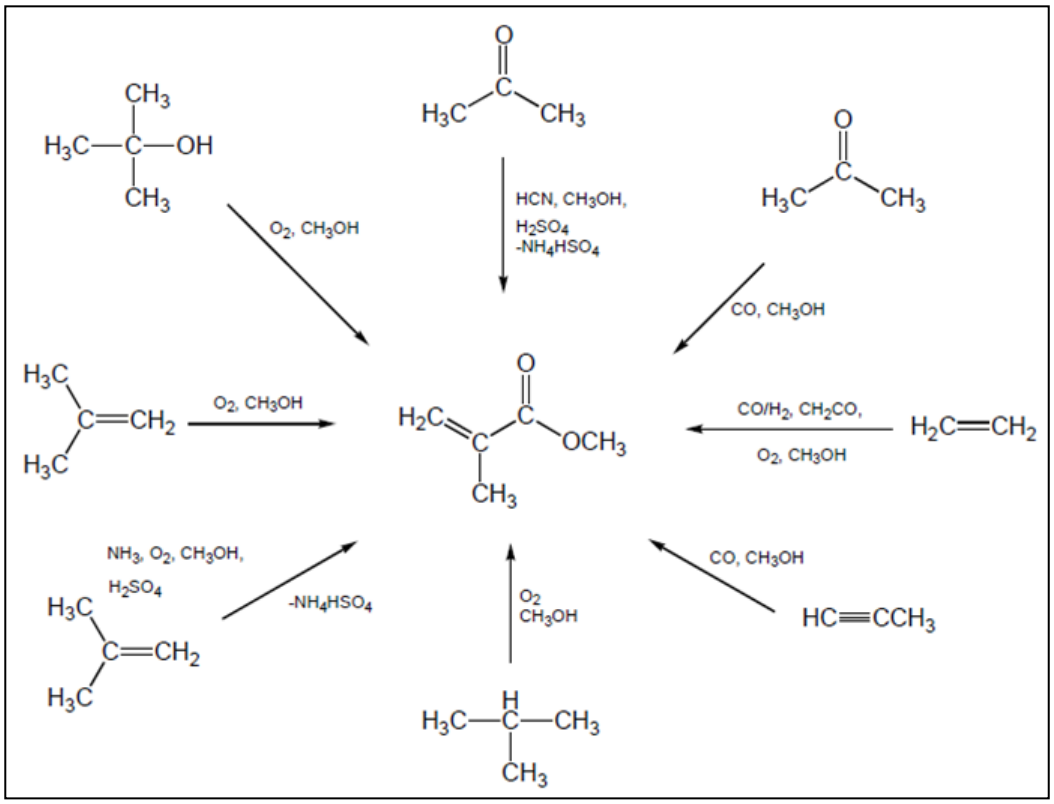

Figure 2.2 Routes to MMA

2.1.3 Global Production of MMA

At the present growth rate, capacity utilization of MMA was estimated exceed 90 percent in United State (Johannes, 2005). World consumption of MMA was over 2 million tons in 2002, valued at approximated US $1 billion. World markets were

currently oversupplied because of the heavy buildup in overseas capacity, especially mainly in China and Southeast Asia. The global market for MMA was forecast to reach a consumption volume of 3.2 million metric tons by the year 2017 (Jose, 2012). Electronics was the fastest growing end-use sector of MMA and PMMA globally, particularly in Asian markets of China, Taiwan and Korea. Persistently rising LCD market had been creating strong demand for the worldwide MMA market. Figure 2.3 shows the global demand and supply of MMA from year 2003 until year 2007 (Koichi and Toshiaki, 2004).

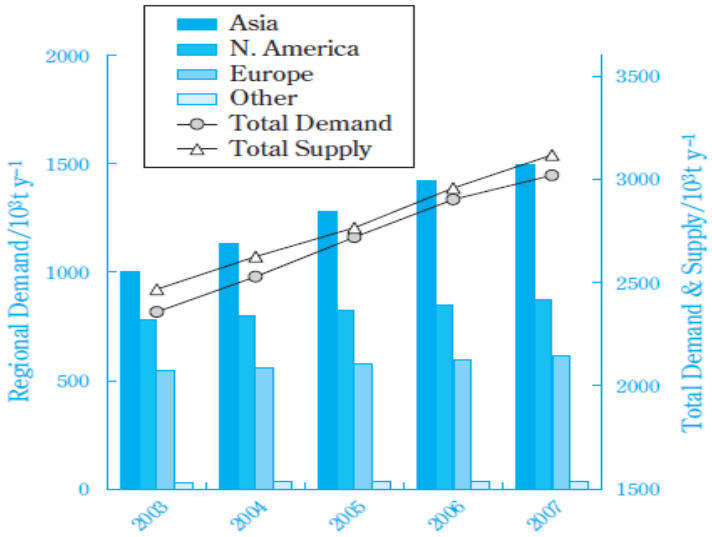

Figure 2.3 Global Demand and Supply of MMA from year 2003 to 2007

2.1.4 Application of MMA and PMMA

MMA was a volatile synthetic chemical that was produced for the use as monomer in the large scale production of polymers and as intermediate for synthesis of other methacrylate esters. MMA principally was used in the production of acrylic plastics and resins for sheeting and molding compounds, which were used in

construction, transportation, consumer products and industrial applications and in making signs (Dormer et al., 1998).

Polymethyl methacrylate (PMMA) was a versatile material and had been used in a wide range of fields due to its clarity, lightweight and resistance to the effect of UV light and weathering. PMMA was used in the lenses of exterior lights of transportation (Kutz and Myer, 2002). PMMA was an important improvement in the design of aircraft windows, making possible such iconic design as the bombardier's transparent nose compartment in the Boeing B-17 Flying Fortress. In orthopedic surgery, PMMA bone cement was used to affix the implants and to remodel the lost bone. It was supplied as a powder and with MMA liquid to yield dough-like cement that gradually hardens (Miller, 1996). Other than that, PMMA in a purified form was used as a matrix for solid state dye lasers (Duarte, 2009).

2.2 Toluene

Toluene (C_7H_8) was a volatile and reactive organic with typical odor as sweet, pungent and benzene-like (NIOSH, 1994). It was an aromatic hydrocarbon that was nearly insoluble in water. However, it was miscible with alcohol, acetone, benzene, ether and others organic solvents (HSDB, 1996). Toluene was widely used in gasoline blending, but also as a solvent for paints, adhesives and industrial feedstock (Parker, 1999). Figure 2.4 shows the structural of toluene.

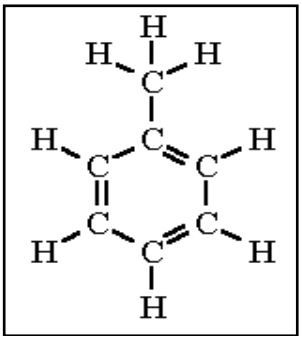

Figure 2.4 Structural of Toluene

2.2.1 Chemical and Physical Properties of Toluene

Table 2.2 below shows the chemical and physical properties of toluene (Budavari et al., 1989; Evonik Industries AG, 2011; Hawley, 1981; Keith and Walters, 1985; NIOSH, 1994; U.S.EPA, 1985; U.S. Air Force, 1989; Verschueren, 1983).

Table 2.2 Chemical and Physical Properties of Toluene

Properties	**Data**
Physical State	Liquid
Appearance	Colourless
Molecular Weight	92.13 g/g mol
Melting Point	-95 ℃
Boiling Point	110.6 ℃
Water Solubility	515 mg/L (20 ℃)
Density	0.87 g/mL (20 ℃)
Vapor Density (air=1)	3.14 g/mL
Vapor Pressure	22 mmHg (20 ℃)
Specific Heat	1.717 KJ/kg K (20 ^{o}C)
Thermal Conductivity	0.141 W/m K
Viscosity	0.59 cP (20 ℃)
Flash Point	4.4 ℃
Henry's Law Constant	6.61x10 atm m^{3}mol
Odor Threshold	2.9 ppm (in air)
Flammability	Inflammable